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LATTICE ENERGY OF KBr AND NaBr AND THE ELECTRON AFFINITY OF BROMINE.

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ABSTRACT. The lattice energies of KBr and NaBr have been experimentally determined from a study of the thermal ionisation of their vapours at temperatures between 1400°C–1650°C. and have been found to be 159K. cals and 176·3 K. cals respectively. By an application of the Born's Cycle the electron affinity of bromine has been calculated to be 80 K. cals. The results are in good agreement with theoretical calculations made from Born's theory, and other experimental data.

1. INTRODUCTION.

The present paper is an extension of the work done by Prof. M. N. Saha and the present author [1] on the "Experimental Determination of the Electron Affinity of Chlorine." Experimental determination of the lattice energies of alkali halides was made by J. E. Mayer [2] in 1930 who made a study of the thermal ionisation of the vapours of the iodides of caesium and potassium at temperatures of the order of 1150°K. He also calculated the electron affinity of iodine from his observations by an application of the Born Cycle. Mayer later on with L. Helmholtz [3] modified his apparatus for working at high temperatures and actually found out experimentally the lattice energies of RbBr and NaCl. They worked with a temperature as high as 1300°K, but even this temperature could not give them many observations with NaCl because it required even higher working temperatures. To meet out this difficulty a successful furnace was designed by Prof. Saha and the author [4] and experiments were made with KCl, NaCl and LiCl for determining the electron affinity of chlorine.[1] In the present paper the method has been extended to determine the lattice energies of KBr and NaBr and from it the value of the electron affinity of bromine has been calculated. Spectroscopic methods have also been used to determine the electron affinity and in this connection the work of Angerer and Müller[5] may be mentioned who observed the absorption spectrum

of the vapours of alkali bromides and attributed the beginning of the continuous absorption to absorption by Br^- and calculated the electron affinity.

The older theories for the lattice energy of ionic crystals gave only approximate results. In 1932, Max Born and J. E. Mayer [6] gave a successful theory for the grating energies of ionic crystals which was in very good agreement with the experimental data available at that time. They took into account the null point oscillation energy, and the effect of Van der Waals cohesive forces in addition to the Coulombian attractive force and a repulsive force between the ions constituting the lattice. The repulsive force has been considered as an exponential function instead of a power of the grating interval as was the case in the old theory.

The lattice energy $\phi_{(r_0)}$ is the energy of the reaction

$$MX_{(solid)} = M^+_{(gas)} + X^-_{(gas)} - \phi_{(r_0)} \qquad \ldots (1)$$

at absolute zero. MX represents an alkali halide. If L_{MX} be the heat of sublimation of the halide at o°K, the heat of dissociation of the gaseous halide into an alkali and a chlorine ion according to the reaction

$$MX_{(gas)} = M^+_{(gas)} + X^-_{(gas)} - Q \qquad \ldots (2)$$

is given by

$$Q = \phi_{(r_0)} - L_{MX}. \qquad \ldots (3)$$

From consideration of the Born Cycle the quantity Q is connected to the heat of dissociation D of the halide, the ionisation potential of the alkali I_0. and the electron affinity E_x of the halogen by the relation

$$Q = D + I_o - E_x$$

Born and Mayer have given the following formula for the grating energy of ionic crystals:—

$$\phi_{(r_0)} = -\frac{\alpha e^2}{r_0} + \frac{C}{r^6} + (1-K)\frac{\rho}{r_0}\left\{\frac{\alpha e^2}{r_0} + \frac{6c}{r_0^6} + \frac{3VT}{N}\left(\frac{\partial p}{\partial T}\right)_V\right\} + E \qquad \ldots (4)$$

where $$K = \frac{(a-1)M'C_2\left(1 + \frac{C_1}{C_2}c^{-\frac{2\delta}{\rho}}\right)e^{(\delta/\rho+1-a)r_0/\rho}}{2M + aM'C_2\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{(\delta/\rho+1-a)r_0/\rho}}.$$

$$C = S'_6C_{+-} + S''_6\frac{C_{++} + C_{--}}{2}$$

$E = \frac{9}{4} h\nu_{max.}$

a = The Madelung number.

ρ = A constant for the alkali halides.

$S_6' = \sum \frac{1}{R^6}$ for the same kind of ions.

$S''_6 = \sum \frac{1}{R^6}$ for different kind of ions.

$\delta = r_- + r_+$ difference between the ionic radii.

M = Number of different kinds of neighbouring ions.

M′ = Number of same kind of neighbouring ions.

$C_{++} = C_1$ = Interaction between two positive ions.

$C_{--} = C_2$ = Interaction between two negative ions.

C_{+-} = Interaction between two oppositely charged ions.

a = a constant quantity for a given crystal.

Helmoltz and Mayer[7] calculated the lattice energies of all the alkali halides according to the above equation and also found the electron affinity of the halogens. Recently their calculations have been revised by M. L. Huggins [8] who has used more recent data for r_+, r_-, compressibilities, Van der Waals attraction constants and other quantities entering into the equation. In table I, the calculated as well as the experimental values for the lattice energy of alkali bromides are given. The heats of sublimation of alkali bromides, the ionisation potential of the alkalies, the heats of dissociation of the alkali bromides and the theoretical as well as experimental magnitude of the electron affinity for bromine are also given in the table.

TABLE I.

Salt	L_{MX}	D	I_ϕ	$\phi_{(r_0)}$ K. Cals.			E_x (K. Cals.)		
	K. Cals.	K. Cals.	K. Cals.	Helmholtz and Mayer.	Huggins.	Experimental.	Helmholtz and Mayer.	Huggins.	Experimental.
Li Br	43·4	102·3	123·8	188·3	189·5		81·2	80·0	
Na Br	51·6	86·0	117·9	174·6	175·5	176·3*	80·9	80·0	79·2[9]
K Br	50·4	90·6	99·5	159·3	161·3	159·7*	81·2	79·2	80·8*
Rb Br	49·0	90·5	96·0	153·5	156·1	151·3[3]	82·0	79·5	84·2[3]
Cs Br	46·9	91·9	89·5	146·3	149·6		82·0	78·7	

* Present paper.

The values for the electron affinity of the other halogens calculated accordin g to Born and Mayer's theory are

Halogen.	Helmholtz and Mayer (K. Cals.)	Huggins (K. Cals.).
Fluorine	95·5	93·4
Chlorine	86·5	85·1
Iodine	74·2	72·1

All the values mentioned above are in good agreement with experimental results. J. E. Mayer [2] found that the electron affinity of iodine is $72{\cdot}6 \pm 2$K. cals. and later on P. P. Sutton and J. E. Mayer [9] obtained a value of $72{\cdot}4 \pm 1{\cdot}5$ K. cals. from another different method. From their experiments on NaCl L. Helmholtz and J. E. Mayer [3] obtained a value of 88·3 K. cals. for the electron affinity of chlorine. M. N. Saha and the present author [1] worked with KCl, NaCl and LiCl and obtained a value of 86·6 K. Cals. In the present investigation on bromine the value obtained is 80 K. Cals. which is in good agreement with the values given in table 1, and also with the value 84·2 K. Cals found by L Helmholtz and J. E. Mayer [3] from their experiments on RbBr.

2. THEORY.

If MBr denotes an alkali bromide molecule, the dissociation process at any temperature can be represented by the following set of equations:—

$$MBr \rightleftharpoons M + Br - D. \quad \ldots (5)$$

$$MBr \rightleftharpoons M^{+} + Br^{-} - Q. \quad \ldots (6)$$

$$M \rightleftharpoons M^{+} + e - I_0. \quad \ldots (7)$$

$$Br^{-} \rightleftharpoons Br + e - E. \quad \ldots (8)$$

$$Br_2 \rightleftharpoons 2Br - D'. \quad \ldots (9)$$

D′ is the heat of dissociation of bromine. The dissociation of diatomic molecules has been theoretically worked out by Gibson and Heitler [10] who have taken into account the translational, rotational, vibrational states of the molecules and also the effect of nuclear spin. If K_1, K_2, K_3, K_4, and K_5 be the equilibrium constants of the reactions represented by the equations (5) to (9) then we have

$$\log K_1=\log \frac{p_M p_{Br}}{p_{MBr}} = -\frac{D}{2{\cdot}3RT} + \frac{3}{2}\log T + \log\left(1-e^{-\frac{h\nu}{kT}}\right) + \log\left[\frac{2^{\frac{3}{2}}K^{\frac{3}{2}}}{\pi^{\frac{1}{2}}Ih}\left(\frac{m_{MBr}}{m_M m_{Br}}\right)^{\frac{3}{2}}\right] \quad \ldots \quad (10)$$

$$\log K_2=\log \frac{p_{M^+}p_{Br^-}}{p_{MBr}} = -\frac{Q}{2{\cdot}3RT} + \frac{3}{2}\log T + \log\left(1-e^{-\frac{h\nu}{kT}}\right) + \log\left[\frac{K^{\frac{3}{2}}}{2^{\frac{3}{2}}\pi^{\frac{1}{2}}Ih}\left(\frac{m_{MBr}}{m_M m_{Br}}\right)^{\frac{3}{2}}\right] \quad \ldots \quad (11)$$

$$\log K_3=\log \frac{p_{M^+}p_e}{p_M} = -\frac{I_0}{2{\cdot}3RT} + \frac{5}{2}\log T + \log \frac{(2\pi m_e)^{\frac{3}{2}}K^{\frac{5}{2}}}{h^3} \quad \ldots \quad (12)$$

$$\log K_4=\log \frac{p_{Br}p_e}{p_{Br^-}} = -\frac{E_x}{2{\cdot}3RT} + \frac{5}{2}\log T + \log \frac{(2\pi m_e)^{\frac{3}{2}}K^{\frac{5}{2}}}{h^3} \quad \ldots \quad (13)$$

$$\log K_5=\log \frac{p^2_{Br}}{p_{Br_2}} = -\frac{D^1}{2{\cdot}3RT} + \frac{3}{2}\log T + \log\left(1-e^{-\frac{h\nu}{kT}}\right) + \log\left[\frac{m^{\frac{3}{2}}K^{\frac{3}{2}}}{4\pi^{\frac{1}{2}}Ih}\right] + \log 8. \quad \ldots \quad (14)$$

I is the moment of inertia of the molecule. The dissociation constants K_1, K_2, K_3, and K_4 are connected by the relation

$$K_2 = \frac{K_1 K_3}{K_4}$$

Also from consideration of Born's cycle we get $E = D + I_0 - Q$ ... (15)

and $$\phi_{(r_0)} = Q + L_{MX} \quad \ldots \quad (16)$$

The magnitude of the dissociation constant K_2 is determined experimentally at different temperatures and from it the value of Q is calculated. As the heats of dissociation and sublimation of the alkali halides and the ionisation potentials of the alkalies are well known the electron affinity of bromine and the lattice energy is easily calculated with the help of equations. (11), (15) and (16)

3. EXPERIMENTAL.

The present work deals with an experimental study of the thermal ionisation of the bromides of sodium and potassium at high temperatures. The salt was heated in an electric furnace and the vapour was allowed to enter a region of high temperature where it suffered dissociation into atoms as well as ions according to the equations (5), (6), (7), (8) and (9). The demountable vacuum graphite furnace

described in a previous paper by M. N. Saha and A. N. Tandon [4] was used for the production of high temperature. The experimental procedure and the internal arrangements inside the furnace have also been described elsewhere.[1] The temperature of the graphite tube was recorded by means of a disappearing filament type of pyrometer capabale of reading temperature accurately within 10°C, the temperature at which the salt vaporised was measured by a nickel-nichrome thermocouple. From the temperature of the furnace the vapour pressure could be easily calculated.

The products of dissociation from the graphite tube escaped through a narrow circular opening, then passed through a limiting diaphragm, and were finally collected by a Faraday cylinder connected to a galvanometer. By giving the Faraday cylinder a small positive or negative potential with respect to the graphite tube (which is always kept at earth potential) the current due to the negative bromine or the positive alkali ions could be easily measured. The partial pressure of the ions could be easily calculated from the magnitudes of the ion currents.

If i_g denotes the current recorded by the galvanometer, the magnitude of the total effusion current i_{M^+} (due to the positive ions) is given by

$$i_{M^+} = \frac{2d^2}{r2} i_g$$

where d is the distance between the effusion hole and the limiting diaphragm, and r the radius of the diaphragm. The effusion current is related to the partial pressure p_{M^+} inside the tube by the relation

$$i_{M^+} = \frac{S}{4} \frac{p_{M^+}}{k'T} c \sqrt{\frac{8k'T}{m\pi}}$$

where S is the area of the effusion hole, T the absolute temperature of the graphite tube, m the mass of ion in absolute units, k the Boltzman constant and e the electronic charge. We have therefore

$$p_{M^+} = \frac{i_{M^+}}{eS} \sqrt{2\pi m_M k'T}$$

Similarly, $$p_{Br^-} = \frac{i_{Br^-}}{eS} \sqrt{2\pi m_{Br} k'T}$$

The experimental value of the dissociation constant K_2 is therefore given by

$$K_2 = \frac{p_{M^+} p_{Br^-}}{p_{MBr}} = \frac{i_{M^+} i_{Br}}{e^2 S^2} (2\pi k'T) \frac{\sqrt{m_M m_{Br}}}{p_{MBr}} \quad \ldots (17)$$

4. RESULTS.

The results obtained for sodium and potassium bromides are given in tables 2, and 3 respectively. In the second column of the tables the vapour pressure of salt at which that observation was taken is given. The vapour pressure of KBr has been calculated from the empirical formula of Fiöch and Rodebush [11]

$$\log p_{mm} = -\frac{8780}{T} + 8{\cdot}2470$$

For NaBr the older formula of von Wartenburg and Albrecht [12] has been used

$$\log p_{atm.} = -\frac{38580}{4{\cdot}57T} + 5{\cdot}0675$$

In the fourth and fifth columns of the tables the magnitude of the positive and negative ion current is given for the diameter of the effusion hole given in the first column. The last three columns contain the values of the equilibrium constant, Q and the lattice energies respectively. The mean values for the lattice energy of KBr and NaBr come out to be 159·7 K. Cals and 176·3 K. Cals respectively. The electron affinity for bromine as calculated with KBr comes out to be 80·8 K. Cals while with NaBr it is 79·2 K. Cals. These experiments therefore give a mean value of 80 K. Cals. for the electron affinity of bromine.

TABLE II

Diameter of the effusion hole (mms.)	Vapour pressure (dynes/cm.^{2})	Temperature of the graphite tube (°C)	$i_{k^+} \times 10^5$ (amps.)	$i_{Br^-} \times 10^5$ (amps·)	$K_2 \times 10^4$	Q K. cals.	$\phi_{(r_0)}$
1·05	44·53	1620	8·853	7·568	93·33	107·4	157·8
,,	78·11	1610	9·044	7·752	55·43	108·7	159·1
,,	28·96	1590	5·714	3·809	45·84	108·2	158·6
,,	12·73	1570	2·879	2·252	30·74	107·6	158·0
,,	19·13	1550	3·273	2.067	17·62	109·2	159·6
,,	85·53	1550	5·078	3·174	11·28	111·3	161·7
,,	38·96	1520	4·121	2·905	18·03	107·3	157·7
,,	20·97	1470	1·668	1·315	5·967	108	158·4
,,	17·85	1460	1·374	1·001	4·369	108·4	158·8
,,	26·89	1435	0.849	0·738	1·303	110·9	161·3
1·17	227·9	1570	11·03	9·99	24·08	109·4	159·8
,,	69·45	1555	4·988	4.357	15·48	110·1	160·5
,,	31·46	1550	3·538	2·692	14·90	109·7	160·1
,,	22·48	1550	2·819	2·435	14·97	109·7	160·1
,,	227·9	1525	9·221	7·60	15·13	108·2	158·6
,,	75·63	1520	3·717	2·819	6·713	110·9	161.3
,,	54·17	1490	2·845	2·308	5·771	109·4	159·8
,,	31·46	1480	1·718	1·358	3·521	110.5	160·9
,,	75·63	1400	1·23	0·948	0·697	119·9	161·3

Average of Lattice energy = 159·7 K. Cals.

TABLE III.

Diameter of the effusion hole (mms.)	Vapour pressure (dynes/cm²)	Temperature of the graphite tube (°C)	$i_{Na^+} \times 10^6$ (amps.)	$i_{Br^-} \times 10^6$ (amps.)	$K_2 \times 10^6$	Q K. Cals.	$\phi(r_0)$
1·17	31·7	1620	9.228	5·895	67·41	126	177·6
,,	14·89	1600	4·86	3·076	39·08	126·7	178·3
,,	66·99	1560	10·13	5·725	33·69	124·4	176·0
,,	52·84	1500	4·184	2·642	7·695	125·3	176·9
,,	66·99	1475	5·064	2·863	7·845	123·4	175·0
,,	52·84	1410	1·64	0·991	1·081	125·2	176·8
,,	94·19	1400	2·312	1·212	1·031	124·7	176·3
1·58	38·64	1640	25·09	17·33	134·4	124·7	176·3
,,	123·1	1600	28·68	21·51	58·49	125·1	176·7
,,	52·84	1555	12·55	8·366	22·67	125.4	177·0
,,	43·55	1540	10·16	7·171	18·92	125	176·6
,,	38·64	1525	9·561	5·975	16·44	122·5	174·1
,,	123·1	1500	11·95	8·067	8·672	124·8	176·4
,,	52·84	1470	5·378	3·885	4·209	123·1	176·7
,,	43·55	1460	5·974	4·183	6·204	123	174·6

Average of Lattice energy = 176·3 K. Cals.

5. DISCUSSION OF RESULTS.

It can be easily seen that the experimental lattice energies for K Br and NaBr are in good agreement with the theoretical values given in table 1. The electron affinity of bromine which has been found to be 80 K. Cals is also in fairly good agreement with the theoretical values and also with the experimental value of L. Helmholtz and J. E. Mayer[3] (84·2 K. Cals). According to theory, the positive and negative ion currents should be inversely proportional to their atomic weights. This relation is satisfied in both the cases within an accuracy of 15%, but a noticeable feature is that in most of the observations this ratio is less than the theoretical value which should be 1·432 for KBr and 1·865 for NaBr. This can only be attributed to the presence of free electrons inside the graphite tube, the effect of which will be to increase the number of negative bromine ions according to equation (8) and to diminish the number of alkali ions according to the equation (7). Evidently these free electrons are the thermally liberated electrons from the graphite tube at that temperature. The current due to these electrons was found to be negligible in comparison to the ion currents. (This was found by performing experiment without any salt in the subsidiary furnace.)

The deviation from the theoretical ratio has also been noticed by Helmholtz and Mayer[3] in their investigations on RbBr and NaCl, but they found that the positive ion current was larger than its theoretical value. For sodium chloride they have taken very few measurements and so nothing decisive can be told. They attribute the abnormal value of the ratio to the formation of an ion sheath round the effusion hole on account of the existence of a contact potential between

the gas inside the oven and the surface surrounding it. The formation of such a sheath will accelerate one kind of ions and retard the other. This explanation appears to be correct but does not seem to account for the increase of one particular kind of ion current.

In the investigation of the electron affinity of chlorine by M. N. Saha and the author it was observed that the positive ion current was much larger than the negative ion current in the case of sodium chloride. It was argued that this diminution of the negative current was due to the formation of molecular chlorine. This interpretation was based on a wrong calculation and cannot be taken as correct. At the temperatures and pressures used in the experiment more than 99% of the chlorine would exist in the atomic state. This can be tested with the help of equation (14). It was thought that in Helmoltz and Mayer's experiment the abnormally large positive ion current was due to this cause on account of working at low temperatures (1300° K), but even at this temperature only 4% of bromine will exist in the molecular state, at the pressures used in the experiment.

The limits of experimental error in such experiments have been thoroughly discussed by J. E. Mayer[2] and later on by Helmholtz and Mayer[3] who showed that the probable error is not more than ±2·5 K. Cals.

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